Structure–reactivity relationships for basic catalysts derived from a $Mg^{2+}/Al^{3+}/CO_3^{2-}$ layered double hydroxide

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The specific activities of catalysts formed by thermal activation of the layered double hydroxide $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5}\cdot 2.6H_2O$ have been determined using 2-methyl-3-butyn-2-ol (MBOH) as an acid/base-selective substrate. Acetone and acetylene were the only reaction products formed over the temperature range 80–150°C, demonstrating that all of the LDH-derived catalysts have highly basic selectivities. Thermal activation below the structural decomposition point of the LDH ($\leqslant 250$°C) afforded catalysts with specific activities approximately an order of magnitude larger than the amorphous metal oxides and crystalline $MgAl_2O_4$ spinel–MgO mixtures formed by thermal activation at 450 and 890°C, respectively. Even the remnant LDH structure formed by partial decarbonation/dehydroxylation at 350°C was substantially more active than the more commonly used metal oxide derivatives.

Keywords: Layered double hydroxides; basic catalysts

1. Introduction

Layered double hydroxides (LDHs) [1,2] of the general type $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$, where A^{n-} is the gallery anion and $x = 0.17$–0.33, have played an important role in the design of heterogeneous catalysts. LDH derivatives of a desired composition typically are formed by co-precipitation of M^{II}, M^{III}, and A^{n-} from aqueous solution and then transformed into mixed metal oxides by thermal decomposition at elevated temperatures. The mixed oxides obtained by LDH calcination exhibit several desirable properties as heterogeneous catalysts, namely, strong basic sites, high surface areas, chemical homogeneity, and good thermal stability. Catalytic applications of the oxides include polymerization of alkene oxides [3,4] and aldol condensations of aldehydes and ketones [5,6]. Also, LDHs containing transition metals (Ni, Co, Cu, Cr or Mn) have been used as precursors of redox catalysts for reforming, nitrobenzene reduction, methanation, methanol synthesis, higher-alcohol synthesis and Fischer–Tropsch chemistry

[7]. These and other applications of LDH-derived catalysts have been reviewed recently by Cavani et al. [7].

Although there have been extensive studies on the use of LDHs as precursors to metal oxide catalysts, relatively little work has been reported on the catalytic properties of LDHs themselves. LDHs intercalated with cobalt(II)phthalocyaninetetrasulfonate [8,9] or polyoxoanions [10–13] recently have been shown to promote oxidative reactions. In these latter materials the active sites are the anions intercalated in the interlayer region of the structure. Also, organic halide exchange reactions producing alkyl bromides and iodides have been catalyzed by LDHs intercalated by Cl^-, Br^- or I^- [14,15].

The present work examines the basic catalytic properties of a hydrotalcite-like $Mg^{2+}/Al^{3+}/CO_3^{2-}$ LDH at temperatures below the structural decomposition point. We also have included in the study a comparison of the reactivity of the metal oxides formed above the decomposition temperature in an effort to obtain structure–reactivity relationships. Until now, basic properties have been investigated only for the thermal decomposition products of LDH carbonates using titration with indicators [16,17], carbon-bound H–D exchange [5] or catalyst testing, such as the condensation reaction of benzaldehyde with ethylacetoacetate [18] or the dehydration–dehydroxylation of 2-propanol [19]. Little or no information is available concerning the basic catalytic activity of the LDH carbonate structure itself. In our study of LDH activity 2-methyl-3-butyn-2-ol (MBOH) was used as an acid–base selective probe molecule. This substrate has been shown recently to form specific conversion products when processed over acidic, basic or amphoteric catalysts [20].

2. Experimental

Synthesis. The LDH-carbonate was prepared by coprecipitation according to Miyata's procedure [21]. A mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (32.00 g, 0.125 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (23.41 g, 0.063 mol) was dissolved in 187 ml of deionized water. The aqueous solution was slowly added with stirring at 40°C to 200 ml of a NaOH solution at pH 10. The pH was maintained at this value by the continuous addition of 0.2 M Na_2CO_3 (molar ratio $CO_3^{2-}/Al^{3+} = 0.7$) and 2 M NaOH aqueous solutions. The LDH suspension was stirred overnight at 70°C. The solid was isolated by centrifuging and then resuspended in 0.1 M Na_2CO_3 (molar ratio $CO_3^{2-}/Al^{3+} = 0.5$) aqueous solution. After stirring for 1 h, the solid was thoroughly washed with deionized water and dried overnight at 80°C. The X-ray powder diffraction pattern showed the expected basal spacing of 7.7 Å [21]. Elemental analysis indicated the Mg^{2+}/Al^{3+} molar ratio to be 2.34. The sodium content was 0.04 wt% and the water content was 17.0 wt% by TGA experiment. Thus, the LDH composition was $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5} \cdot 2.6H_2O$.

Characterization. The solid sample was dissolved in 20% (v/v) HNO_3, and the metal elements were analyzed by ICP emission spectroscopy at the College of Veterinary Medicine, Michigan State University. X-ray diffraction patterns were recorded on a Rigaku diffractometer using Cu K_α radiation (45 kV and 100 mA) and a scan speed of 4° 2θ/min. The divergent and scattering slits were set at 0.5° and the receiving slit was 0.3°. The diffraction patterns for thermally activated samples were recorded at room temperature after heating the sample under a flow of nitrogen for 2 h. The activated samples were transferred quickly to the X-ray sample compartment to avoid rehydration. Thermogravimetric experiments were carried out on a Cahn TGA System model 121 under a flow of nitrogen gas. The temperature was ramped at a rate of 5°C/min from 30 to 900°C. BET-N_2 surface areas were determined on a Quantasorb Jr. Sorption System. The samples were placed inside a horizontal quartz tube in the center section of a tube furnace and heated under a flow of nitrogen gas at the desired temperature for 2 h. After this step, the samples were transferred to the BET sample cell and outgassed under vacuum at room temperature for 1 h. The sample calcined at 890°C for 4 h was outgassed at 150°C for 1 h before the surface area measurement.

Catalytic reactions. 2-methyl-3-butyn-2-ol (MBOH) was purchased from Aldrich Chemical Company and used without further purification. MBOH conversion was carried out in a micro reactor equipped with an on-line Perkin-Elmer 8500 gas chromatograph. The liquid reactant was placed in a saturator at 24°C and the vapor was introduced into the reactor by means of a He flow of 20 ml/min. A 150 mg quantity of the LDH with a particle size between 150 and 75 μm was placed in the reactor and activated at 80–450°C under a He flow for 2 h. A separate furnace was used for sample activation at 890°C. The reactor was adjusted to the desired temperature and the MBOH stream was introduced at a flow rate of approximately 1.2 mmol/h [22]. The products were analyzed by gas chromatography after reaching steady state conditions within 2 h reaction time. The chromatograph was equipped with an FID detector and a 6″ × 1/8″ o.d. stainless steel column packed with 3% SP-1500 on Carbopack B (80/120 mesh).

3. Results and discussion

The thermogravimetric curve for $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5}\cdot 2.6H_2O$, shown in fig. 1, indicated the loss of water occurs in two principal steps. The weight loss between 30 and 200°C can be attributed to the release of interparticle pore water [2]. Between 200 and 300°C, the weight loss is due to the liberation of water molecules located in the LDH galleries [23,24]. The interlayer water corresponds to a molar H_2O/CO_3^{2-} ratio of approximately 4. In the range 300–650°C the LDH undergoes decarbonation and dehydroxylation reactions which release carbon dioxide and water and form metal oxides.

The XRD patterns (fig. 2) for samples activated at representative temperatures corroborate previous assignments for LDH-carbonate thermodecomposition. The

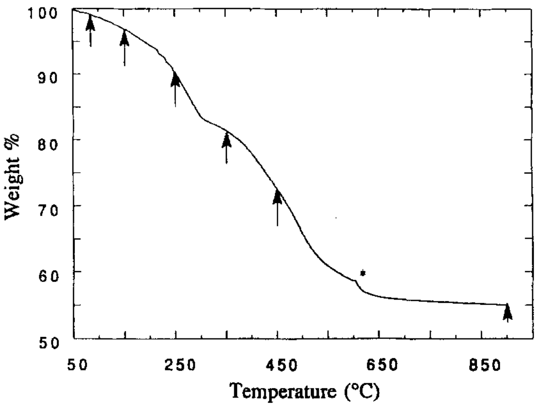


Fig. 1. Thermogravimetric analyses (TGA) curve for $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5}\cdot 2.6H_2O$. Arrows identify the temperatures used to generate catalysts for MBOH conversion. The feature indicated by * is an instrument artifact.

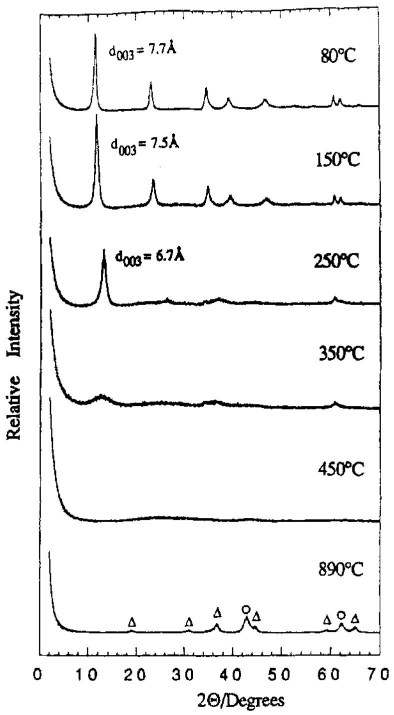
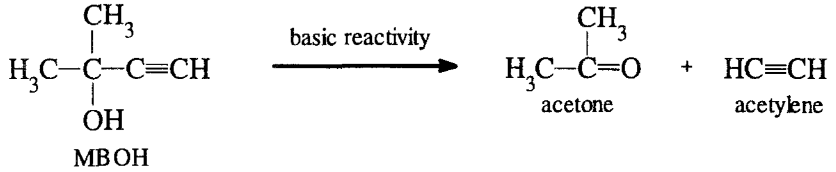


Fig. 2. X-ray powder diffraction patterns for catalysts formed by the thermal activation of $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5}\cdot 2.6H_2O$. Diffraction peaks corresponding to MgO and $MgAl_2O_4$ spinel [24,27] are labeled ○ and △, respectively.

LDH basal spacing decreases by only 0.2 Å when the sample dried at 80°C is heated at 150°C for 2 h, indicating the retention of gallery water. A more substantial change in basal spacing (~ 1 Å) is observed at 250°C owing to the dehydration of the gallery surface. At 350°C the sample could be characterized as a partially decarbonated/dehydroxylated or remnant LDH phase of very low crystallinity. The LDH phase disappears completely at 450°C and the material can be described as an amorphous mixed oxide solution. Sato et al. [24] attributed the amorphous oxide to the composition $Mg_{(1-x)/(2+x)}Al_{2x/(2+x)}[\,]_{x/(2+x)}O$, where [] is a cation vacancy. According to Reichle et al. [23], the amorphous oxide formed at this temperature retains the particle morphology of the LDH. At 890°C, the XRD pattern indicates the appearance of a $MgAl_2O_4$ spinel and crystalline MgO. This latter result is consistent with earlier observation of spinel formation at elevated temperature [25].

The conversion of 2-methyl-3-butyn-2-ol (MBOH) over each of the above LDH-derived catalysts afforded exclusively equimolar amounts of acetone and acetylene, as expected for a base-catalyzed reaction [20],



$$H_3C-C(CH_3)(OH)-C\equiv CH \xrightarrow{\text{basic reactivity}} H_3C-C(CH_3)=O + HC\equiv CH. \quad (1)$$

MBOH acetone acetylene

Interestingly, magnesium–aluminium oxides formed by LDH-carbonate activation at 450°C have been reported by Nakatsuka et al. [17] using titration methods to possess acid sites with $4.8 > H_0 \geqslant 4.0$. Also, MacKenzie et al. [19] and Kelkar et al. [26] used 2-propanol conversion to study acid/base reactivity of metal oxides formed by LDH-carbonate and nitrate decomposition, respectively. The 2-propanol reaction produced mainly acetone and minor amounts of propene, which they also attributed to acid catalytic sites. However, we observed essentially no acid-catalyzed alkane formation (<0.2%) arising from the conversion of MBOH over our thermally activated LDH catalysts. If acid sites are indeed present in our LDH-derived catalysts, they are at least two orders of magnitude less active toward MBOH than the basic sites giving rise to acetone and acetylene formation.

As shown by the specific activities reported in table 1, all of the LDH-derived catalysts exhibited MBOH conversions >93% at a reaction temperature of 150°C. However, when the temperature is reduced to 110 or 80°C, important structure-dependent differences in reactivity can be distinguished. Most significantly, the specific activities at 80°C clearly show that the LDH carbonate activated below the structural decomposition temperature (≤250°C) is an order of magnitude more active than the metal oxides generated at 450 or 890°C. Even the remnant LDH structure represented by the partially decarbonated/dehydroxylated sample at 350°C is substantially more active than the metal oxides formed by thermal decomposition.

Table 1
Conversion over catalysts formed by thermal activation of LDH carbonate

Activation temp. (°C)	Structural assignment	Surface area ($m^2 g^{-1}$)	Reaction temp. (°C)	Conversion (%)	Specific activity ($mmol/m^2 h$)
80	LDH containing pore and interlayer water	–	80	22.4	0.020
150	LDH without pore water	89	80	47.7	0.044
			150	100	>0.093
250	anhydrous LDH	91	80	25.1	0.024
			150	99.9	>0.097
350	partially decarbonated LDH	107	80	4.7	0.0043
			110	64.6	0.060
			150	93.5	~ 0.086
450	amorphous oxide	180	80	4.5	0.0028
			110	38.9	0.024
			150	99.5	>0.061
890	spinel and MgO	83	80	2.7	0.0026
			110	39.9	0.038
			150	99.1	>0.096

Crystalline LDHs have not been previously reported to possess basic catalytic properties. In fact, freshly precipitated (unactivated) LDH carbonates have been characterized as being inactive for certain basic catalyzed reactions [3,5]. It is likely that surface water inhibits substrate access to the basic sites on the LDH surface. For instance, the LDH activated at 80°C, where pore water is present, is less active than the sample activated at 150°C.

The strength and origin of the basic sites in crystalline LDH carbonates remains to be investigated. The activity may be controlled in part by the basic hydroxyl groups associated magnesium sites in the brucite-like layers. Also, the CO_3^{2-} ions at external surfaces may function as strong basic sites when separated from sites of positive charge on the LDH surface. Regardless of the origin of the basic activity, however, the results of the present work clearly demonstrate that crystalline LDHs can be useful materials for low temperature base-catalyzed conversions of organic molecules. Future studies will investigate the dependence of LDH basic catalysis on exchangeable anion and the possible applications of these materials for remediation of contaminated environments and pollution control.

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